Plutonium Speciation in the WIPP: An Update of the Safety Case for Plutonium Containment

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Waste Isolation Pilot Plant (WIPP) Transuranic Program

The Waste Isolation Pilot Plant (WIPP) transuranic repository remains a cornerstone of the U.S. Department of Energy's (DOE) nuclear waste management effort. Waste disposal operations began at the WIPP on March 26, 1999 but a requirement of the repository license is that the WIPP needs to be recertified every five years for its disposal operations. The WIPP received its second recertification in November 2010 and a third recertification is in process. Research by the Los Alamos Actinide Chemistry and Repository Science team [1-4] is centered on the speciation of key actinides under WIPP-specific conditions to improve the robustness of current models and quantify the conservatisms in the current assumptions being made is continuing.

Plutonium, for most of the duration of repository performance (10,000 y), is the most important actinide from the point of view of potential release as well as public perception and concern. Overall, the ranking of actinides, which has not changed since CRA-2009, is:

$$Pu \approx Am >> U > Th >> Np \approx Cm$$

From the point of view of oxidation state, rather than nuclide, the ranking with respect to release is:

$$An(III) > An(IV) >> An(VI) >> An(V)$$

Herein we summarize new data that support the safety case for plutonium containment, specifically as Pu(III) and Pu(IV) species, in the WIPP repository. In this recertification cycle, longer-term Pu-Fe interaction studies were completed, thorium solubility studies in brine were performed, and the performance assessment (PA) approach to define the contribution of colloids to the actinide source term was re-examined and updated. These recent data [1-5] continue to extend our understanding of high ionic-strength actinide chemistry.

Status of the WIPP Project

- 14+ years of safe operation until February 2014.
- 21 waste storage sites in the US cleaned up
- Over 10,000 TRU shipments received
- Over 78,000 m^3 of waste emplaced
- Six panels are full and panel 7 is being filled
- Emplaced waste will contain approximately 10,000 kg Pu and 51,000 metric tons of iron
- Second Recertification granted by the EPA in November 2010; the third recertification (2014) is now underway.
- Repository is in a prolonged shutdown as of February 2014 until two safety issues are resolved.
  - Truck fire safety incident on February 6, 2014
  - Small release of Am/Pu on February 14, 2014

SAFETY CASE APPROACH FOR PLUTONIUM CONTAINMENT

The core safety case for the containment of plutonium in the WIPP is the self-sealing property of the bedded salt formation. This self-sealing is relatively rapid (a few hundred years or less) and will permanently isolate the TRU waste. Under this scenario, geologic isolation is achieved since the repository will not likely saturate leading to essentially no significant release of TRU.

Why are TRU/Pu Studies Needed?

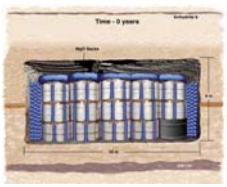
- Low-probability human intrusion scenarios that could lead to brine saturation of the waste in the repository and the formation of a mobile actinide concentration and subsequently release actinides to the accessible environment need to be addressed.
- The approach used to specifically model plutonium behavior, should brine-inundation occur, was established for the initial license application and has been reviewed/accepted by the EPA regulator three times (initial license and two recertification reviews). The key features of this approach are:
  - Once self-sealing occurs, the repository will rapidly become anoxic and the reduced iron phases will establish a strongly reducing brine chemistry environment. This is augmented by microbial processes that also remove oxygen and may reduce metals/actinides directly.
  - Pu(V) and Pu(VI) do not persist in the WIPP due to these reducing conditions. It is, however, recognized that they may be present as transients due to radiolytically-induced localized oxidizing zones.
  - The oxidation-state distribution of plutonium is fixed, by expert opinion, to be Pu(III) in ~50% and Pu(IV) in ~50% of the PA vectors. This is considered to be a conservative assumption because Pu(IV) should predominate and Pu(III) is ~ 10 times more soluble.
  - The concentration of mobile plutonium species is determined as the solubility of Pu(III) and Pu(IV) phases and the corresponding colloidal species that are associated with each oxidation state.
  - Th(IV) is used as an oxidation-state invariant analog for Pu(IV). Am/Nd(III) are used as the oxidation-state invariant analog for the solubility of Pu(III). In both cases, the Pitzer model is used to calculate solubility and these model calculations are confirmed by site-specific solubility measurements.

Updated Pu Inventory Data

Repository time		2033 (0 years)	2133 (100 years)	3033 (1000 years)	12033 (10,000 years)
Pu	Ci	2.02×10^6	1.03×10^6	7.24×10^5	5.00×10^5
	Kg	1.20×10^4	1.19×10^4	1.16×10^4	9.12×10^3
% of Actinide Activity		74%	62%	83%	99.8%

Plutonium Isotope	Activity in Ci (% of Total)	Mass in Kg (% of Total)
^{238}Pu	6.01×10^5 (29.7)	34.7 (0.29)
^{239}Pu	5.74×10^5 (28.4)	9.13×10^3 (76.3)
^{240}Pu	1.75×10^5 (8.6)	762 (6.4)
^{241}Pu	6.63×10^5 (32.8)	6.38 (~0)
^{242}Pu	8.09×10^3 (0.40)	2.04×10^3 (17.0)
^{244}Pu	0.0101 (~0)	0.567 (~0)

Waste Material	Total Mass (Kg)
Iron-Based metals/alloys	4.91×10^7
CPR (Cellulosic/Plastic/Rubber)	1.54×10^7
MgO (Engineered Barrier)	5.14×10^7
Organic Ligands (Citrate)	7.78×10^5
Organic Ligands (EDTA)	3.76×10^2



In the WIPP safety case, the reliance is on the site geology, and not the survivability/ integrity of the container, to attain TRU waste isolation. The container is to aid shipping and emplacement.

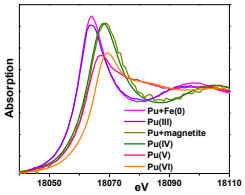
Scientific Challenges for Pu in the WIPP environment

1) Establish the oxidation state distribution of Pu under WIPP-related conditions
2) Measure the oxidation-state specific source term: Solubility and colloidal species

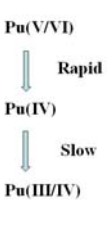
Plutonium Redox Chemistry in the WIPP

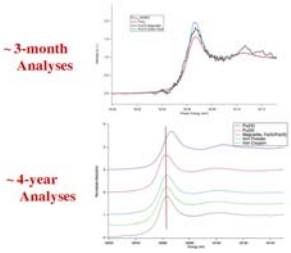
Under the expected conditions in the WIPP, plutonium is predicted to exist predominantly as Pu(III) and Pu(IV) species. In the performance assessment, it is assumed that Pu(IV) exists in all "oxidizing" vectors (50% of the time) and Pu(III) exists in all "reducing" vectors (also 50% of the time) – see table and notations below.

There are two redox pathways that will sustain lower plutonium oxidation states that are likely to occur in the WIPP should brine inundation occur. These are reduction of higher-valent plutonium by reduced iron (Fe(0) or Fe(II)) and indirect or direct effects of microbial activity. In the presence of reduced iron, we have shown that reduction occurs under all anoxic conditions that have been investigated. Measured E_h values between -100 mV and -250 mV are observed. Plutonium (IV) and Pu(III) are observed in both the solids present (XANES) and the aqueous phase (TTA extraction). In most cases, Pu(III) is predominant. The redox trends due to microbial effects should also facilitate the reduction of Pu(V/VI) to Pu(III/IV) . This, although implied in work we have completed with U(VI) and Np(V) has not been demonstrated in high ionic strength conditions – although we are expecting to do this in the near future.



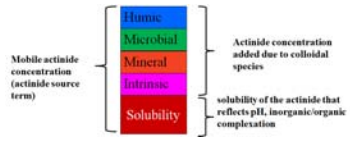
~ 5 year data obtained cryogenically at SLAC showing Pu(III) in Fe(0) and Pu(IV) when magnetite was the predominant iron phase

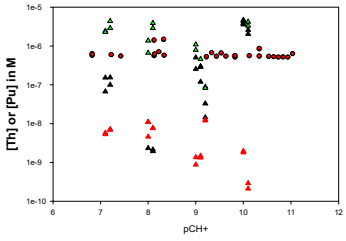




Plutonium Solubility and Speciation in the WIPP

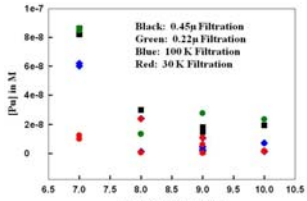
The solubility of plutonium is modeled using a combination of Am(III)/Nd(III) data and Th(IV) data as analogs. Current WIPP-specific calculations are shown below. The speciation of Pu(III) will be dominated by EDTA/Citrate complexation and the assumed concentration of these organic complexants defines the current predicted solubilities. This is confirmed experimentally in our Nd^{3+} studies. The solubility of thorium(IV) is not significantly affected by pH and the range of carbonate and organic complexants expected in the WIPP. Plutonium concentrations expected are however 100 to 1000 times lower in Fe dominated systems. Strong association with very fine Fe phases is there appears to be a greater tendency towards colloid formation with Pu (vs. Th). Plutonium studies are underway to further evaluate the colloidal contribution and overall solubility as a function of brine and ionic strength.





Comparison of Th (red circles) and Pu (triangles - green unfiltered, black 0.2 micron filtered, and red 30K-filtered) Solubility Data

Size distribution of plutonium in long-term solubility studies (colloidal Fe is present)



Calculated Actinide Solubility: Historical Trends

Actinide Oxidation State, and Brine	CRA-2004 PABC (M)	CRA-2009 PABC (M)	CRA-2014 PA (M)
III, GWB	3.87×10^{-7}	1.66×10^{-6}	2.59×10^{-6}
III, ERDA-6	2.88×10^{-7}	1.51×10^{-6}	1.48×10^{-6}
IV, GWB	5.64×10^{-8}	5.63×10^{-8}	6.05×10^{-8}
IV, ERDA-6	6.79×10^{-8}	6.98×10^{-8}	7.02×10^{-8}
V, GWB	3.55×10^{-7}	3.90×10^{-7}	2.77×10^{-7}
V, ERDA-6	8.24×10^{-7}	8.75×10^{-7}	8.76×10^{-7}

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[5] Appendix SOTERM-2014, Actinide Chemistry Source Term. Title 40 CFR Part 191Subparts B and C Compliance Recertification Application 2014. for the Waste Isolation Pilot Plant; and Van Soest, G. 2012. *Performance Assessment Inventory Report – 2012* (PAIR 2012). INV-PA-12, LANL-CO\Inventory Report, Los Alamos, NM: Los Alamos National Laboratory (2013).